values of log $a_{HSO_4^-}$, used in the derivation of log $a_{H_3SO_4^+}$, become available. It is doubtful, however, that the linear behavior would be affected by using accurate log $a_{H_3SO_4^+}$ values rather than the log $X_{H_3SO_4^+}$ values used here. Using log $X_{H_3SO_4^+}$ means that an additional activity coefficient term, log ($f_{H_3SO_4^+}f_{HSO_4^-}$), is present in eq 2. This term could well cancel to zero, since one species is increasing and the other decreasing (see Figure 1). The observed similarity of slopes for the correlations with log $a_{H_2SO_4}$ and log $X_{H_3SO_4^+}$ in Figure 3 is a point in favor of this possibility.

It would appear that the Buncel–Strachan mechanism[8] for the azoxybenzene rearrangement, involving general acid catalysis, is correct. This reaction requires the strongest acids of the system, *i.e.*, H_2SO_4 and $H_3SO_4^+$, in order for the reaction to go. The solvated proton H_3O^+ is *not a strong enough acid* to catalyze the reaction. Undissociated H_2SO_4 (K_a = 2550)[30] is a much better proton donor than H_3O^+ (K_a = 1)[31] at these acidities. According to Figure 1, H_3O^+ should be the better proton donor, because of greater concentration, only at acidities below about 67% H_2SO_4.

In connection with the above is an interesting observation that the Wallach rearrangement does not go in perchloric acid,[32] even at an H_0 of −10.2 (78% $HClO_4$).[33] Now it should be borne in mind that perhaps $HClO_4$ is not such a strong acid regarding oxygen protonation (Wallach rearrangement) as it is toward nitrogen protonation (H_0 scale measurement). However, one could argue as follows. At this H_0 in perchloric acid the stoichiometric concentration of H_2O is greater than that of $HClO_4$, which is not the case in H_2SO_4. Thus all the acidity is due to solvated protons; the undissociated $HClO_4$ concentration is negligible,[34] both for this reason and because as a stronger acid than H_2SO_4 it is more dissociated. So the rearrangement does not go, since H_3O^+ is not strong enough to catalyze the reaction, and the strong acid species $HClO_4$ is not present in high enough concentration.[34] It would undoubtedly be present at $HClO_4$ concentrations around 100% acid,[35] but as yet no one has had the temerity to carry out mechanistic studies in the 100% $HClO_4$ medium.

(30) P. A. H. Wyatt, *Trans. Faraday Soc.*, **56**, 490 (1960).
(31) Since the reaction is $H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$.
(32) R. Bolduc, E. Buncel, R. A. Cox, and R. B. Kitzul, submitted for publication.
(33) K. Yates and H. Wai, *J. Amer. Chem. Soc.*, **86**, 5408 (1964).

Summary

This study probably represents the least ambiguous demonstration so far presented of general acid catalysis in the 80–100% H_2SO_4 acidity region. The utility of correlations between log rate and log species activity is clear. Other examples of general acid catalyzed reactions are undoubtedly amenable to similar treatment (the Beckmann rearrangement in the 100% H_2SO_4 region is one possibility[36]) and will hopefully be explored in future publications.

Acknowledgments. This work was supported by a grant from the National Research Council of Canada administered by Professor Erwin Buncel, under whose stimulating sponsorship this study was initiated. Helpful discussions with Professor Ross Stewart of the University of British Columbia are also acknowledged.

(34) Extrapolation of Duerst's data[35] shows that the undissociated perchloric acid concentration probably only becomes significant above 82% $HClO_4$. The stable solid hydrate at 84.8% has the formula $H_3O^+ClO_4^-$.
(35) R. W. Duerst, *J. Chem. Phys.*, **48**, 2275 (1968).
(36) M. I. Vinnik and N. G. Zarakhani, *Russ. J. Phys. Chem.*, **38**, 491 (1964).

Solvolysis of 8-Vinyl-*exo*-8-bicyclo[3.2.1]octyl 3,5-Dinitrobenzoate. Evidence for Stabilization by Carbon–Carbon Hyperconjugation in the Transition State for Formation of a Tertiary Allylic Cation

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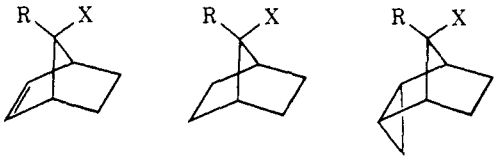
Abstract: The high exo/endo reactivity ratio (8000) for acetolysis of the epimeric 8-bicyclo[3.2.1]octyl tosylates may derive from preferential "vertical" stabilization of the transition state for ionization of the exo tosylate by carbon–carbon hyperconjugation. Support for this suggestion is found in the observation that a high reactivity ratio is maintained and that high product stereospecificity is manifest in the solvolysis of the epimeric 8-vinyl-8-bicyclo[3.2.1]octyl 3,5-dinitrobenzoates (k_{exo}/k_{endo} = 515). Since the "leveling capacity" (10^8) of the vinyl group exceeds the exo/endo rate ratio exhibited by the secondary tosylates by a factor of 10^4, incorporation of a vinyl substituent at the site of ionization should engender complete cessation of neighboring group participation if such participation were nonvertical in nature.

A comparison of the solvolytic behavior of a series of 7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates (**1a**) with that of their norbornyl analogs (**2a**) has prompted Gassman and Fentiman[1] to suggest that there exists a definite upper limit to the amount of stabilization an aryl group can provide by means of delocalization of

(1) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **92**, 2549, 2551 (1970); **91**, 1545 (1969).

positive charge at a benzylic position. They suggest further that introduction of an aryl substituent at the



1 2 3

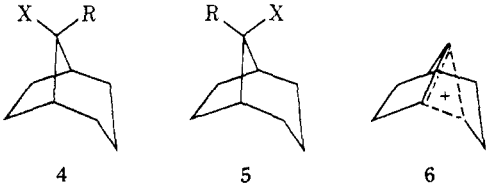
a, R = aryl; X = *p*-nitrobenzoxy
b, R = H; X = tosyloxy
c, R = *p*-anisyl; X = *p*-nitrobenzoxy
d, R = vinyl; X = 3,5-dinitrobenzoxy (ODNB)

displacement site of a system which can undergo solvolysis with neighboring group participation (*e.g.*, **1**) will cause cessation of neighboring group participation if the ability of the aryl group to stabilize the incipient cation exceeds the stabilization furnished by the neighboring group. If, however, the stabilization afforded by the neighboring group exceeds the upper limit to the capacity of the aryl to provide stabilization through conjugation, all characteristics of neighboring group participation will be maintained. In this event the effect of aryl substitution will be manifest only in the ratio of the rate of solvolysis of the system capable of neighboring group participation (*e.g.*, **1**) to that of a suitable model system incapable of such participation (*i.e.*, **2**). Since the full stabilizing influence of the aryl group is available in the latter system, the effect of aryl substitution is to "level" this rate ratio. Gassman and Fentiman suggest that this "leveling capacity" is defined by the ratio $10^{11}/(k_{1a}/k_{2a})$, since 10^{11} is the rate of solvolysis of the parent *anti*-7-norbornenyl tosylate (**1b**) relative to its norbornyl analog (**2b**).[2] Additional support for these conclusions and for their generality was inferred from the solvolytic behavior of **3c**, in which the double bond of **1c** has been replaced by an endo fused cyclopropane ring as the participating neighboring group. Since the "leveling capacity" of the *p*-anisyl group $[10^{11}/(k_{1c}/k_{2c})]$ was found to be *ca.* 3×10^{10}, and since the anchimeric assistance (k_{3b}/k_{2b}) provided by the cyclopropane ring is *ca.* 10^{14},[3] one would predict that this ratio should be "leveled" to *ca.* 3×10^{3} by introduction of a *p*-anisyl substituent. The observed ratio (k_{3c}/k_{2c}) is 3.8×10^{3}.

The fact that double bond participation and conjugative stabilization appear to be competitive rather than cooperative during solvolysis of **1** strongly implies that, at least to a great extent, stabilization by the double bond is a "nonvertical" process, *i.e.*, a process which must involve some distortion of nuclear positions of the participating group. Some support for this view may be drawn from the conclusion that the nmr spectra of the 7-aryl-7-norbornenyl cations whose aryl groups are less electron releasing than *p*-anisyl indicate that these cations "are bridged in the ground state with extensive ehybridization at C-7 which precludes any significant $\sigma-\pi$ overlap between C-7 and the phenyl ring"[4] and have a geometry distorted with respect to the parent hydrocarbon in such a way as to place C-7 in closer proximity to C-2 and C-3.[5] It seems very likely that the apparent constancy of the "leveling capacity" of the *p*-anisyl substituent on interchange of double bond (**1c**) and cyclopropane ring (**3c**) as neighboring groups implies that cyclopropane participation is nonvertical also.

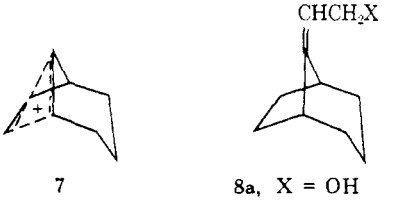
By contrast, as Traylor, *et al.*,[6] make clear, a neighboring group which exerts its influence by a vertical process should act cooperatively with a conjugated substituent such as aryl. In such a case, we conclude, the "leveling capacity" for the conjugated substituent ascertained from the ratio $10^{11}/(k_{1a}/k_{2a})$ would overestimate the ability of the substituent to diminish the impact of participation by the neighboring group. We report here the results of experiments designed both to test this hypothesis and, in an admittedly tautological fashion, to probe for the manifestation of carbon–carbon hyperconjugation[7] in transition states leading to highly stabilized cations.

Acetolysis of the epimeric 8-bicyclo[3.2.1]octyl tosylates[8] (**4a** and **5a**) exhibits an exo/endo rate ratio (k_{4a}/k_{5a}) of *ca.* 8×10^{3}. Since this system is relatively free of steric bias (*vide infra*) and since the rate of the endo tosylate **5a** is accurately anticipated by the Foote–Schleyer correlation,[9] acetolysis of the exo tosylate **4a** must be accompanied by some form of anchimeric assistance. Foote and Woodward[8] attribute this assistance to "carbon participation" and suggest the possible intervention of the bridged ion **6** as a consequence of this participation. Similar assistance to solvolysis of the endo tosylate **5a** would be precluded, according to this view, by an increase in steric strain of sufficient magnitude to offset any electronic stabilization manifest in the transition state leading to the bridged ion **7**. This interpretation, of course, ascribes the anchimeric assistance in the solvolysis of **4a** to a nonvertical process.



4 5 6

a, R = H; X = tosyloxy
b, R = vinyl; X = ODNB
c, R = vinyl; X = OH



7 8a, X = OH
b, X = ODNB

(2) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, 79, 505 (1957).

(3) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. S. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); J. S. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

(4) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2347 (1972).

(5) H. G. Richey, *et al.*, *J. Amer. Chem. Soc.*, **92**, 3784 (1970).

(6) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971), and previous papers in this series therein cited.

(7) For an elaboration of the inherent differences in vertical and nonvertical processes, as well as the criteria by which carbon–carbon hyperconjugation is adjudged a vertical process, see ref 6.

(8) C. S. Foote and R. B. Woodward, *Tetrahedron*, 20, 687 (1964).

(9) C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); P. v. R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

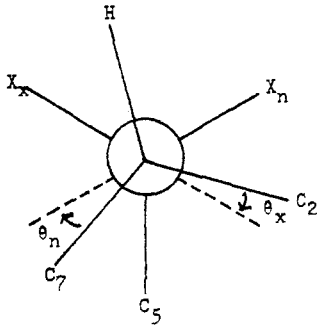


Figure 1. Newman projection along the C_1–C_8 bond of the epimeric 8-bicyclo[3.2.1]octyl tosylates. The dotted lines are linear extensions of the C_8–X bond, and as such represent the axis of the rear lobe of the atomic orbital utilized by C_8 to form this bond. For endo tosylate **5a**, X_n = tosylate and X_x = H. For exo tosylate **4a**, X_x = tosylate and X_n = H. Dihedral angles (θ) are approximate ($\pm 5°$) and are measured clockwise from the C–C bond.

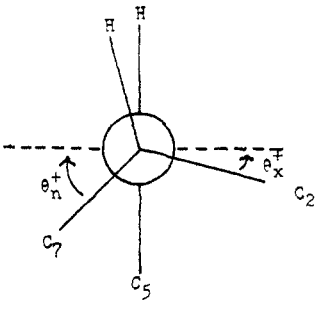


Figure 2. Newman projection along the C_1–C_8 bond of the 8-bicyclo[3.2.1]octyl cation. The dotted line represents the axis of the p orbital at C-8. Dihedral angles (θ^+) are approximate ($\pm 5°$) and are measured clockwise from the C–C bond.

Recent *ab initio* molecular orbital calculations[10] which indicate that carbon–carbon hyperconjugation is a significant factor in the determination of carbonium ion stabilities, coupled with the demonstration by Traylor and coworkers[6] that carbon–carbon hyperconjugation can be identified experimentally in nonsolvolytic reactions as an authentic vertical process, permit an alternate explanation of the high exo/endo rate ratio for solvolysis of **4a** and **5a**.

Maximum stabilization by carbon–carbon hyperconjugation is realized only when the axes of the hyperconjugating σ bond, the intervening σ bond, and the developing p orbital at the ionization site share a common plane, *i.e.*, when the dihedral angle defined by these three axes ($\theta^{\ddagger}$) is zero.[6,10] With specific reference to the 8-bicyclo[3.2.1]octyl system, this condition would be realized if $\theta^{\ddagger}_n$ were zero for ionization of the endo tosylate and if $\theta^{\ddagger}_x$ were zero for ionization of the exo tosylate (Figures 1 and 2). Since, in the transition state for ionization, the hybridization of the orbital originally bearing the leaving group must be intermediate between *ca.* sp^3 (ground state) and pure-p (cation), $\theta^{\ddagger}$ must be intermediate between θ (Figure 1) and θ^+ (Figure 2). For solvolysis of the endo tosylate **5a**, therefore, $20° < \theta^{\ddagger}_n < 50°$, and for solvolysis of the exo tosylate **4a** $15° > \theta^{\ddagger}_x > -15°$. Since $\theta^{\ddagger}_n$ deviates widely from the optimal dihedral angle for carbon–carbon hyperconjugation, while $\theta^{\ddagger}_x$ must closely approximate the optimal angle, we suggest that solvolysis of exo tosylate **4** may well be accelerated by this vertical process, but that endo tosylate **5** cannot be so accelerated. This provides an alternate rationale to at least a portion of the exo/endo rate ratio exhibited by **4** and **5**.

The ratio of the rate of solvolysis of 7-vinyl-*anti*-7-norbornenyl 3,5-dinitrobenzoate (**1d**) to that of its norbornyl analog (**2d**) is 1100 (100°, 70% aqueous acetone).[11] Therefore the "leveling capacity" of the vinyl group as defined by Gassman and Fentiman[1] is *ca.* 10^8 ($10^{11}/1.1 \times 10^3$). Since this exceeds the exo/endo rate ratio for acetolysis of **4a** and **5a** (8000) by *ca.* 10^4, the vinyl group should provide sufficient conjugative stabilization to "level" completely the rates of solvolysis of the epimeric 8-vinyl-8-bicyclo[3.2.1]octyl 3,5-dinitrobenzoates (**4b** and **5b**) and to cause complete cessation of "carbon participation" in solvolysis of these tertiary, allylic derivatives, *if such participation is nonvertical in nature.*

Results and Discussion

Exo alcohol **4c** is the sole tertiary alcohol formed on solvolysis of endo dinitrobenzoate **5b**.[11a] It was separated from its primary allylic isomer by glc and converted to the dinitrobenzoate **4b** in the usual manner. The configuration at C_8 for epimers **4c** and **5c** was assigned on the basis of an analysis of their lanthanide shifted proton nmr spectra.[12] An agreement factor (R) less than 0.09 was found for each epimer utilizing the structure assigned.[13]

The rate of solvolytic disappearance of **4b** in 70% aqueous acetone was followed spectrophotometrically and good first-order rate plots were obtained using experimental infinity values of absorbance: $k_1 \times 10^5$ sec^{-1} = 12.0 (61.5°); 28.9 (70.0°); 345 (100°, extrapolated); $\Delta H^{\ddagger}$ = 20.4 kcal/mol; $\Delta S^{\ddagger}$ = −15.7 eu. The experimental infinity value of absorbance, taken as the value after approximately 5 solvolytic half-lives, was found to be 30% of the initial absorbance. This suggested that solvolysis of **4b** is accompanied by return to a dinitrobenzoate which is essentially inert under the reaction conditions. This conclusion was confirmed by a thorough product study at 70°; three products were found: exo alcohol **4c** (60%), primary alcohol **8a** (12%), and primary dinitrobenzoate **8b** (28%). Neither endo alcohol **5c** nor its dinitrobenzoate (**5b**) was found in the product mixture, although as little as 5% of either could have been detected.[14]

Comparison of the first-order solvolytic rate constant for *exo*-dinitrobenzoate **4b** with that of its endo epimer (**5b**, $k_{100°} = 0.67 \times 10^{-5}$ sec^{-1})[11a] yields an exo/endo rate ratio of 515.

Since dinitrobenzoates **4b** and **5b** undoubtedly differ slightly in their gound-state free energies, this gross rate ratio must be corrected to eliminate the influence

(10) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 5935 (1972); see also R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *ibid.*, **94**, 6223 (1972), and references therein cited.

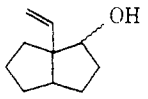
(11) (a) T. J. Mason, M. J. Harrison, J. A. Hall, and G. D. Sargent, *J. Amer. Chem. Soc.*, **95**, 1849 (1973); (b) G. D. Sargent, J. A. Hall, M. J. Harrison, W. H. Demisch, and M. A. Schwartz, *ibid.*, **91**, 2379 (1969).

(12) M. R. Willcott, III, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742 (1972); R. E. Davis and M. R. Willcott, III, *ibid.*, **94**, 1744 (1972).

(13) Professor M. R. Willcott, personal communication.

(14) For a detailed discussion of the factors which prevent assigning a lower maximum to the per cent of **5b** or **5c** which may be present, together with a description of the method of analysis, see ref 11a.

of steric bias. An attempt to obtain this free energy difference directly by acid-catalyzed equilibration of alcohols **4c** and **5c** failed, since both rearrange to a mixture of two isomeric alcohols, which were not identified conclusively, but which are presumably the epimeric bicyclo[3.3.0]octyl alcohols **9**. Examination of models



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reveals the only apparent source of differing ground-state free energies for **4b** and **5b** to be the difference in steric compression energies for a vinyl group oriented axially to a cyclohexane ring (**4b**) and a similarly oriented 3,5-dinitrobenzoxy group (**5b**). The conformational *A* value for vinyl appears not to have been measured experimentally, but must certainly be no greater than ethyl (1.8 kcal/mol) and may be closer to carboxyl (1.2 kcal/mol).[15] Since the *A* value for *p*-nitrobenzoxy, a perfectly adequate model for 3,5-dinitrobenzoxy, is 1.0 kcal/mol,[15] the difference in ground-state free energies for **4b** and **5b** in all probability lies in the range 0.2–0.8 kcal/mol. In the transition state for solvolysis of both esters, the unfavorable compression is relieved: for **5b** through an increase in the C–O bond length,[16] and for **4b** by the reorientation of the vinyl group which accompanies rehybridization at C-8. If one makes the reasonable assumption that this relief is complete in both transition states, then the gross solvolysis rate ratio must be divided by a factor of 1.17–4.65 to compensate for the higher ground-state free energy of **4b**. Even if one assumes the highest extreme in this range, one is left with a sterically unbiased **4b**/**5b** rate ratio of 122!

Both this high reactivity ratio and the high stereospecificity associated with product formation at the ionization site are characteristics normally associated with neighboring group participation. This preservation of participation, even in the face of the apparently overwhelming "leveling capacity" of the vinyl group, strongly suggests that the stabilization results in this case from a vertical process, and we tentatively assign carbon–carbon hyperconjugation by the C_1–C_2 and C_4–C_5 σ bonds as the source of this stabilization.

Experimental Section

8-Vinyl-*exo*-8-bicyclo[3.2.1]octanol (4c). 8-(2′-Ethylidenyl)bicyclo[3.2.1]octane 3,5-dinitrobenzoate (**8b**)[11a] (450 mg) and urea (200 mg) were dissolved in 80 ml of 70% (v/v) aqueous acetone. This solution was sealed in several glass ampoules which were heated at 100° for 16 hr. The tubes were cooled to room temperature and opened, and their combined contents was diluted with 700 ml of diethyl ether. The resulting solution was washed with saturated NaCl (3 × 100 ml), saturated $NaHCO_3$ (100 ml), and water (5 × 100 ml) and then dried over anhydrous $MgSO_4$. The volume of solution was reduced to a small volume on a rotary evaporator. Separation of alcohol **4c** from its isomer **8a** was accomplished by glc on a 5 ft × 0.25 in. column packed with 15% SE-30 on 60–80 mesh Chromosorb W at 175° with a flow rate of He carrier gas of *ca.* 30 ml/min.

8-Vinyl-*exo*-8-bicyclo[3.3.1]octyl 3,5-Dinitrobenzoate (4b). To a solution of 37.2 mg (0.244 m*M*) of alcohol **4c** in 1 ml of dry pyridine at 0° was added 65 mg (0.282 m*M*) of 3,5-dinitrobenzoyl chloride. The resulting solution was stirred for 2 hr at 0°, allowed to warm to room temperature, and stirred for an additional 0.5 hr. The reaction mixture was poured into *ca.* 20 ml of ice–water. The aqueous phase was extracted with ether (4 × 20 ml); the combined ether extracts were washed with ice-cold 3% HCl (2 × 20 ml) and saturated NaCl (25 ml) and then dried over anhydrous $MgSO_4$. The solid which resulted from evaporation of the ether at reduced pressure was recrystallized from ether–petroleum ether to yield 56 mg (67%) of a white solid: mp 150–152°; nmr (δ, CCl_4) 9.10 (s, 3 H, aromatic), 6.83, 6.65, 6.53, and 6.35 (1 H, 1′-vinyl), 5.6 and 5.35 (m, 2 H, 2′-vinyl), 2.90 (broad s, 2 H, bridgehead), 2.20 → 1.20 (m, 10 H). *Anal.* Calcd for $C_{17}H_{18}N_2O_6$: C, 58.98; H, 5.20; N, 8.09. Found: C, 58.78; H, 5.03; N, 8.14.

Kinetic Measurements. Dinitrobenzoate **4b** (3–3.5 mg) was dissolved in 20 ml of 70% aqueous acetone and the resulting solution was dispensed into 18 glass ampoules in such a way that each ampoule contained just over 1 ml. The ampoules were maintained at constant temperature (±0.05°), withdrawn one at a time at appropriate intervals, cooled to room temperature, and opened. Exactly 1 ml of solution was withdrawn and added to exactly 10 ml of Spectrograde hexane. The resulting solution was washed with saturated $NaHCO_3$ (2 × 5 ml) and saturated NaCl (2 × 5 ml). The absorbance at 220 nm of the hexane solution was determined directly using a Cary 15 spectrophotometer. After the absorbance had dropped to a value of *ca.* 30% of its initial value it decreased by only minute increments at longer reaction time. Using an "infinity" value of 30% of initial absorbance, good straight lines were obtained for plots of log $(A-A_\infty)$ *vs.* t. Best values for the rate constant were obtained by utilizing a computer program which treats A_∞ as an adjustable parameter to obtain the best linear least-squares fit of the experimental data. In all cases the value of A_∞ which gave this best fit was found to be 30 ± 5% of the initial absorbance.

Product Studies. Dinitrobenzoate **4b** (*ca.* 70 mg) was solvolyzed in 70% aqueous acetone for 3 hr (4.5 half-lives) at 70° and the products were worked up as described for the preparation of alcohol **4c** above. The nmr spectrum of the crude oil obtained from the solvolysis showed peaks at δ 9.10 characteristic of dinitrobenzoate esters and δ 4.05 characteristic of the primary alcohol **8a**. The region δ 5–7 and the upfield region of the spectrum were consistent with that to be expected for a mixture of alcohols **4c** and **8a** and dinitrobenzoate **8b**. Even at maximum amplification, no resonance at δ 5.65 (characteristic of dinitrobenzoate **5b**) or at δ 5.88 (characteristic of alcohol **5c**) was observed. Control experiments indicated that as little as 5% of either **5b** or **5c** present in the reaction mixture could have been detected in this manner.

Trituration of the crude product with cold pentane gave a solution of product alcohols essentially free of dinitrobenzoate esters. Analysis of this solution by glc utilizing the conditions above indicated the presence of only alcohols **4c** and **8a** in the molar ratio 5:1.

The residue from the pentane trituration was taken up in a small volume of a solution prepared by diluting 20% aqueous KOH with an equal volume of ethanol and stirred for 2 hr at room temperature. The resulting solution was diluted with 10 times its volume of water and extracted with a small volume of pentane. The pentane extract was washed several times with saturated NaCl, dried, concentrated to small volume, and analyzed by glc. Once again, only peaks with retention times identical with those of alcohols **4c** and **8a**, with the latter strongly predominating, were obtained.

Since the dinitrobenzoate present in the original mixture must be *ca.* 95% primary ester **8b**, since the ratio of ester **8b** to primary alcohol **8a** is found to be 2.3:1 from the ratio of the integrated nmr signals at δ 9.1 and δ 4.05, and since the ratio of tertiary alcohol **4c** to primary alcohol **8a** is found to be 5:1 by glc, one calculates the following relative yields for the solvolysis reaction: tertiary alcohol **4c**, 60%; primary dinitrobenzoate **8b**, 28%; primary alcohol **8a**, 12%.

Acknowledgment. We are grateful to the Mobil Oil Company for financial support in the form of an unrestricted grant in aid and to Professor M. Robert Willcott, III, for the analysis of the lanthanide shifted nmr spectra of the epimeric 8-vinyl-8-bicyclo[3.2.1]-octanols. T. J. M. thanks the Science Research Council for an SRC/NATO Fellowship.

(15) E. L. Eliel, *et al.*, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 44.

(16) Reference 15, pp 84–85; see also H. Kwart and T. Takeshita, *J. Amer. Chem. Soc.*, **86**, 1161 (1964).